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(71) Applicant : **Alko Ltd.**
P.O. Box 350
SF-00101 Helsinki (FI)

(72) Inventor : **Rha, Chokyun**
285 Commonwealth Avenue
Boston, MA 02118 (US)
Inventor : **Timonen, Maritta**
Kantelettarentie 8E 57
SF-00420 Helsinki (FI)

(74) Representative : **Collier, Jeremy Austin Grey et al**
J.A.Kemp & Co., 14 South Square, Gray's Inn
London WC1R 5LX (GB)

(54) **Additive for paper and its use.**

(57) A mixture of polymers derived from degradation of a polysaccharide derivative is used during the paper-making process as a means of strengthening the paper and as a dewatering agent.
Paper is either coated or impregnated with a mixture of the polymers.

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This invention pertains to the field of paper, pulp and textile making and their chemistry.

Of the many raw materials used by the paper industry, cellulose fibers have occupied the dominant position for nearly 2000 years. The techniques of paper making are known worldwide and the basic principles have not changed. Despite great improvements in papermaking, however, procedures for strengthening cellulose fibers in the papermaking process are often expensive, time consuming, and environmentally questionable.

The kraft or sulfate process is probably the most extensively employed method to produce strong cellulose fibers. The active ingredients in pulping wood to its fibrous state are sodium hydroxide and sodium sulfide, in a strong alkaline solution. The process generates objectionable smells from the sodium sulfide produced during the process. Kraft pulps are dark in color, difficult to bleach and very strong.

Nevertheless, cellulose fibers obtained from the pulping process are generally unsuited for paper making and must first be refined. With given pulps, final paper properties are largely controlled by the type and extent of refining action employed. A variety of additive materials can be introduced to the paper-making pulps, commonly called "furnish", during stock preparation. Fillers such as clays, or calcium carbonate are used for the control of sheet opacity and for other reasons. Dyes are used extensively for color control and other additives such as wet-strength agents, and defoamers are used as needed.

For the most part, however, operations designed to increase the strength and/or other physical properties of paper take place subsequent to the paper making operation and are called "off-machine converting". These converting operations are highly complex and include embossing, coating, waxing, laminating, impregnating, saturating, currogating, and printing. For example, food packaging has led to extensive paper utilization with the paper often being coated, waxed, resin-impregnated, or combined with other foils and films. A relatively simple and inexpensive method of improving the paper making process and increasing the stiffness and ultimate strength of paper is needed.

SUMMARY OF THE INVENTION

It is an object of the invention to provide materials that improve the properties of paper, pulp and textile products.

It is a further object of the invention to provide a simplified paper-making process by improving the dewatering and draining properties of paper pulp.

It is yet another object of the present invention to provide degradation products of polysaccharide derivatives which are useful as strengthening and dewatering agents for treating paper products or materials.

The invention discloses the manufacture of novel paper materials comprising treating paper with water soluble or water suspendable mixtures of relatively low molecular weight polymers. The polymers are obtained by degrading polysaccharide derivatives, most preferably starch and cellulose derivatives.

The invention further pertains to paper products coated or impregnated with water soluble or water dispersable mixtures of relatively low molecular weight polymers obtained by degrading polysaccharide derivatives. Most preferably these mixtures are obtained by degrading starch or cellulose derivatives.

In accordance with the invention, there is provided a water soluble or water dispersable mixture of polymers derived from a degraded polysaccharide derivative, the mixture of polymers having an average degree of polymerization in the range of about 3 to about 500, usually 3 to 300, preferably 5 to 100, and more preferably 5 to 50. The most preferred polysaccharide derivative comprises starch or cellulose. The polysaccharide derivative may be degraded by enzymatic, chemical, physical, or mechanical agents/mechanisms. In embodiments where an enzyme preparation is utilized to perform the degradation, the enzyme preparation is typically selected from the group of polysaccharide degrading enzymes. In the case of starch derivatives, enzymes such as amylases or pullulanases and mixtures thereof are suitable.

In embodiments where degradation of a polysaccharide derivative is to be effected by chemical or physical means, chemical hydrolysis, chemical oxidation and heat treatment are preferred mechanisms for achieving the desired polymeric mixtures according to the invention.

By conventional means, a polymer or an initially degraded polysaccharide derivative mixture may be further separated into fractions of polymers of differing average chain lengths, e.g. using chromatographic techniques. The viscosity of the various fractions will vary with the degree of average chain length of the polymers contained within in a fraction. Depending on the particular paper product application, one or more fractions are selected from an initial polymeric mixture having a viscosity (average chain length) which is most appropriate for the particular application.

The method of strengthening paper comprises treating the paper with a water soluble or water dispersable mixture of relatively low molecular weight polymers, which polymers are obtained by degrading polysaccharide derivatives, most preferably starch and cellulose.

The method of enhancing the dewatering properties of paper pulp comprises treating the pulp with a water

soluble or water dispersable mixture of relatively low molecular weight polymers, which polymers are obtained by degrading polysaccharide derivatives, most preferably starch and cellulose.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a force-distance curve of Whatman No. 1 filter paper treated with carboxylmethyl cellulose hydrolyzate.

Figure 2 is a force-distance curve of Whatman No. 1 filter paper dipped in distilled water.

Figure 3 is a force-distance curve of untreated Whatman No. 1 filter paper.

Figure 4 shows results of drainage tests on furnish treated with carboxymethyl cellulose (CMC) hydrolyzate (•), carboxymethyl cellulose (o), carboxymethyl starch (CM starch) hydrolyzate (□), carboxymethyl starch (CM starch) (Δ), and untreated furnish (□).

Figure 5 shows results of drainage tests on furnish/calcium carbonate mixtures treated with carboxymethyl cellulose (CMC) hydrolyzate (•), carboxymethyl cellulose (o), carboxymethyl starch (CM starch) hydrolyzate (□), and carboxymethyl starch (CM starch) (□).

DETAILED DESCRIPTION OF THE INVENTION

This invention describes paper materials treated with the degradation product of a polysaccharide derivative and methods therefor. The term "polysaccharide" refers to a polymeric carbohydrate having a plurality of repeating units comprised of simple sugars. The term "polymeric" or "polymer" is meant to include both oligmeric and polymeric units and, specifically, those polysaccharides having more than four repeating monomeric simple sugar units.

The C-O-C linkage formed between two joined simple sugar units in a polysaccharide chain is called a glycosidic linkage, and continued condensation of monosaccharide units will result in polysaccharides. The most common polysaccharides are amylose and cellulose, both made up of glucose monomers. Amylose is a major constituent of starch and glycogen. Cellulose is the major structural component of plants. Other polysaccharides useful in this invention have a straight chain or branched polymer backbone including one or more sugar monomers. These polysaccharides include those having sugar monomers such as glucose, galactose, arabinose, mannose, fructose, rahmnose, and xylose.

Preferred polysaccharides useful in the article and methods of this invention are cellulose and starch. Nevertheless, examples of other such polysaccharides with branched or straight backlones are carragenan, pullulan, pustulan, laminarin, scleroglucan, alginate, guar gum, gum arabic, inulin, pectin, whelan, rhamsan, gellan, xanthan, zooglan, methylan, chitin, cyclodextrin and chitosan.

The term "derivative" is meant to define polysaccharides according to this invention that are substituted. Preferably, the polysaccharide derivative starting material has a degree of derivatization or substitution of between about 0.1 and about 3.0. "Degree of substitution" refers to the number of derivative groups (e.g. carboxymethyl, hydroxypropyl) per monomer unit in the polysaccharide backbone (branch or straight chain backbone). A degree of substitution of 0.2 means, for example that there is about one derivative substituent for every five monomer units in the polysaccharide backbone. A degree of substitution of three would mean there are three derivative substituents per every monomer unit in a polysaccharide chain. Typical substituents comprise one or more of sulfate, carboxylic acid (found in carragenan, alginate, pectin), carboxylic ester, pyruvic acid (found in pectin, xanthan gum, zooglan, and methylan), carboxymethyl, hydroxypropyl, methyl, methylethyl, hydroxyethyl, hydroxyethylmethyl and the like.

Specifically, carboxymethyl starch can be degraded enzymatically to produce corresponding carboxymethyl starch hydrolyzates. Other typical suitable starch derivatives include hydroxypropyl, methylethyl and hydroxyethyl starches. The substituents are typically bonded to a starch glucose monomer unit at the 2, 3 and 6 positions. Most typically a starch starting material comprises between about 1% to 85% amylose and about 15% to 99% amylopectin.

Cellulose derivatives are commercially available. Such exemplary products as methylcellulose (MC, Methocel MC, 64630, Fluka Chemie AG, CH-9470 Buchs, Switzerland), hydroxypropylmethylcellulose (HPMC, H-9262, Sigma Chem. Co., St. Louis, MO) and carboxymethyl cellulose (CMC 7MFD, Blanose, Hercules Chem. Co., 92507 Rueil-Malmaison Ceder, France) all have a degree of substitution between 0.1 and 3. Hydroxypropyl celluloses are also commercially available and suitable for use.

As described more fully herein, such polysaccharide derivatives may be degraded to polymeric mixtures of average degree of polymerization (DP) between about 5 and about 500 by enzymatic, chemical, physical or mechanical agents/means. The polymeric mixtures are generally referred to as a "hydrolyzate". The term "degraded" refers to the procedure whereby polysaccharide derivatives are broken down into smaller polymeric

units.

Exemplary enzymes for use in degrading certain of the above described polysaccharide derivatives are pectinases, lyases, lysozymes, xanthanases chitinases and laminarases. Exemplary enzymes which are suitable for degrading cellulose derivatives are various cellulases. They can be produced from a multitude of different microorganisms such as strains of Trichoderma, Aspergillus, Penicillium, etc. A selected microorganism strain is grown by conventional means in a suitable medium such that the cellulases are produced, the microorganism is separated from the medium, the medium is collected and typically concentrated and dried. Cellulase preparations suitable for use herein are, e.g. the commercially available cellulase preparations designated as the Econase series as produced by Alko Ltd., Helsinki, Finland.

A polysaccharide derivative may be hydrolyzed by treating a polysaccharide derivative with a solution of acid. Typical acid treatment solutions might contain acids such as sulphuric acid, hydrochloric acid, phosphoric acid, or mixtures of the foregoing. The concentration of the acid in the treatment solution and the treatment time and temperature may vary depending on the degree of degradation of the polysaccharide derivative which is desired. In any event where an acid hydrolysis treatment is utilized, the acid concentration and the treatment time and temperature is selected to produce a mixture of polymers having an average DP of between 5-500.

A selected polysaccharide (e.g. starch or cellulose) derivative may be degraded by oxidation with such agents as chlorine, oxygen or hydrogen peroxide. Such oxidative treatments and reaction conditions are well known in the art. It may also be possible to use physical methods like heat or mechanical shear treatment or sonication when cleaving the chain backbone of polysaccharide derivatives.

Whatever conventional chemical (hydrolytic, oxidative or otherwise) or physical treatments are employed, the conditions and the degree of treatment are selected such that the polymeric mixture resulting from the initial treatment has an average DP of between about 3 and about 500, and contains less than about 25% preferably less than 10% by weight of mono- and di-saccharides.

Enzymes which may be used with respect to paper products prepared or coated with degraded starch derivatives, are various amylolytic enzyme preparations. They can be produced from a multitude of different microorganisms such as strains of Bacillus, Klebsiella, Clostridium, Aspergillus, Rhizopus. Typical commercially available enzyme preparations suitable for use herein are amylolytic preparations (such as alpha and beta amylases), pullulanases, and cyclodextrin glycosyltransferases (CGTase).

The polymers described above are used in the method of the invention to improve the properties of paper products and to strengthen paper products. In its broadest embodiment, the method comprises preparing a polymeric mixture of substituted polysaccharides having an average degree of polymerization (DP) in the range of 5-500. Next, the mixture is then contacted with paper for a period of time sufficient to treat the paper with the polymer mixture.

This invention relates more specifically to a paper or paper product treated with water soluble or dispersable mixture of polymers derived from a polysaccharide derivative. The polymeric mixtures are characterized by having an average degree of polymerization (DP) in the range of about 5-500. Preferably, the DP range is between 7-200.

The terms "paper" and "pulp products" are intended to include a variety of products made from cellulose, synthetic or other fibers, such products being recognized by those skilled in the art as paper, boards, construction paper. In addition, these terms refer to articles prepared from cellulose, synthetic, or other fibers or filamenatous materials such as those used in the textile industry. Specific examples include felted or matted sheets of cellulose fibers, formed on a fine wire screen from a dilute water suspension, and bonded together as the water is removed and the sheet is dried. These terms may also include sheet materials produced from other types of fibers, particularly mineral or synthetic fibers, formed and bonded by other means. These terms also include liquified or semi-solid mixtures of pulped fibers, commonly called "furnish", to which is added various materials such as fillers (clays, calcium carbonate), dyes, wet-strength agents and the like during the typical paper-making process.

Methods of paper manufacture include the basic steps of pulping fibers, refining the pulp by addition of various materials, as described below, forming the paper on mesh screens, and drying the matted fibers.

The polymer mixtures can be applied after the paper is made, in the so-called "off-machine converting" procedures. The mixtures can be applied using methods well known in the art such as dipping, spraying, and rolling.

Not wishing to be bound by any theory, it is believed that the polysaccharide derivative mixture thus prepared coats the surface of the paper and becomes fixed thereon by attraction between the polysaccharide mixture and the polysaccharide components of the paper including by physical forces such as hydrogen binding, Van der Waals forces and the like. The low molecular weight polymers of the invention are aligned along the cellulose, or other fibers. As a result, the intermolecular attraction per unit length increases, facilitating the quality of the final product and improving the processability of the paper or pulp product.

The polymeric mixtures can also be incorporated into the paper furnish during pulp defining procedures. In this embodiment, the mixture of degraded polysaccharides can be incorporated into the pulp furnish along with other dyes, colorants, wet-strength agents (agents capable of increasing the strength of wet or suspended materials), defoamers, and the like. In this procedure, the polysaccharides will become impregnated into the matrix of the paper fibers.

The term "treated" or "treatment" are intended to include means or methods for contacting paper products with the polymeric mixtures so that at least one effect of such contact is to strengthen the paper, coat or impregnate the paper, improve the paper or pulp handling properties during manufacturing, improve the paper or pulp handling properties during manufacture, and/or increase the dewatering capacity of the paper pulp. Examples of methods of treatment include the two methods of introducing the polymer derivatives of the invention to the paper or paper products described above.

Paper produced according to the method of this invention may be stronger than non-treated paper. Moreover, treated paper may less water spreading than untreated paper. Furnish treated with the polymers of the invention show an increased rate of dewatering during the early stages of draining.

This invention will now be more particularly described using the following examples.

Example 1: Preparation of a Starch Precursor Hydrolyzate

Starch derivative hydrolyzates may be prepared from starch derivatives as defined above by an enzymatic hydrolysis utilizing an amylolytic preparation having α-amylase as the main active hydrolytic agent such that only insignificant amounts of mono- and disaccharides are produced. The hydrolysis procedure is generally carried out by dissolving the starch derivative in water, adjusting the pH and the temperature to the value suitable for the enzyme activity, adding the enzyme to the solution and allowing the enzyme to react for a suitable time. After the enzyme reaction, the enzyme is inactivated by heating the solution up to about 100°C and the hydrolyzate product is concentrated and dried. The average degree of polymerization (DP) of the products formed by such a hydrolysis is less than 500 as determined by the reducing end group measurement, according to Somogyi, M. J. Biol. Chem. 195, 19-33, (1952). The specific conditions suitable for and the specific time sufficient to secure the desirable hydrolysis may be readily determined for each selected starch derivative and each selected enzyme preparation.

Similarly, where degradation is carried out using chemical or physical means, the average DP of the oligomers is less than 500.

60 g of carboxymethyl starch (CM starch) derived from potato starch (Primojel; Avebe, 9607 PT Foxhol, The Netherlands) was mixed in 1200 ml of water. The temperature of the mixture was raised to 80°C and the suspension was mixed continuously. About 1.5 ml of amylase (Ban 120L, Novo, Industri A/S, Novo Alle, 2880 Bagsvaerd, Denmark) diluted 1/50 by volume was added to the suspension mixture. After hydrolysis of about 30 minutes the enzyme was inactivated by heating (100°C, 10 min.). The hydrolyzate was then freeze-dried.

The hydrolyzate's value of reducing sugars was 0.28%. The viscosity of a 5% by weight suspension of the hydrolyzate, measured using Haake-Rotovisco RV 12 viscometer with sensor systems NV; (Karlsruhe, Federal Republic of Germany) at 25 °C was 57 mPa.s using the shear rate of 692 l/s. The viscosity of the unhydrolysed raw CM starch material was 106 mPa.s (25°C, 692 l/s).

Example 2: Preparation of a Cellulose Precursor Hydrolyzate

Cellulose derivative hydrolyzates may be prepared from soluble cellulose derivatives as discussed above by an enzymatic hydrolysis utilizing a cellulase preparation having endo-1, 4-beta-glucanase as the sole active hydrolytic agent. The average degree of polymerization (DP) of the polymers formed by such a hydrolysis is less than about 500, and thus the viscosity of solutions of the hydrolyzate is reduced significantly compared to the viscosity of solutions of the unhydrolysed cellulose derivatives. The specific conditions suitable for and the specific time sufficient to secure the desired hydrolysis may be readily determined for each selected cellulose derivative and each selected enzyme preparation.

Similarly in other embodiments of the invention where degradation is carried out using chemical or physical means, the average DP of the polymers is less than 500 and the viscosity of the resulting mixture is significantly reduced.

Example 3: Preparation of Specific Cellulose Derivative Enzyme Hydrolyzates

a. Methylcellulose hydrolyzate

30 g of methylcellulose (MC, Methocel MC, 64630, Fluka Chemie AG, CH-9470 Buchs, Switzerland) was mixed in 31 of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to 40°C. 0.3 ml of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1680 nkat from which the beta-glucosidase activity was removed chromatographically (as described above) was added to the solution. After hydrolysis for 24 hours the enzyme was inactivated by heating (90°C, 15 min.). The hydrolyzate solution was subsequently cooled and freeze-dried.

The hydrolyzate product contained less than 0.5% by weight of glucose and cellobiose.

b. Hydroxypropylmethylcellulose hydrolyzate

20 g of hydroxypropylmethylcellulose (HPMC, H-9262, Sigma Chemical Company, St Louis, MO, U.S.A.) was mixed in 1 l of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to 40 °C. 0.24 ml of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1340 nkat from which the beta-glucosidase activity was removed chromatographically (as described above) was added to the solution. After two hours another 20g of hydroxypropylmethylcellulose was added to the solution. After the hydrolysis of 22 hours the enzyme was inactivated by heating (90°C, 15 min.). Finally the hydrolyzate solution was cooled and freeze-dried.

The product contained less than 0.05% by weight of glucose and cellobiose.

c. Carboxymethylcellulose hydrolyzate

(i) Hydrolysis with Trichoderma reesei derived enzyme preparation

20 kg of carboxymethylcellulose (CMC 7MFD-type, a cellulose gum, also designated by the tradename Blanose and available from Hercules Chemical Company, 92507, Rueil-Malmaison Ceder, France; 7MFD designates a medium viscosity, food grade carboxymethylcellulose having 7 out of 10 glucose units substituted with carboxymethyl) was mixed in 320 l of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to 40°C. About 0.27 l of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1,780,000 nkat from which the beta-glucosidase activity was removed chromatographically (as described above) was added to the CMC solution. After one hour another 23 kg of CMC was added to the solution. After hydrolysis of 23 hours the enzyme was inactivated by heating (90°C, 15 min.). Finally, the hydrolysis solution was concentrated by conventional evaporating and spray-drying.

The product contained less than 2% by weight of glucose and cellobiose. When the same hydrolysis was carried out with the original cellulase enzyme preparation of Trichoderma reesei-fungus, the amount of produced glucose and cellobiose was above 5% by weight.

(ii) Hydrolysis with Aspergillus and Penicillium derived enzyme preparations

The enzyme preparations selected were commercially available Cellulase AP 3 (Amano Pharmaceutical Co., Ltd., Nagoya, Japan) produced using an Aspergillus strain and Cellulase CP (Sturge Enzymes, North Yorkshire, England) produced using a Penicillium strain. Carboxymethylcellulose hydrolyzates were prepared as described in Example c(i), except that 30g of CMC-7MFD was used in 1 l of water, and the amounts of enzymes added were 0.028 g of Cellulase AP 3 (having a total endo-1, 4 beta-glucanase activity of 1350 nkat) and 0.048 g of Cellulase CP (having a total endo-1, 4 beta-glucanase activity of 1350 nkat). The viscosities and molecular weight distributions of the hydrolyzates produced by either cellulase were similar to the hydrolyzate produced with enzymes derived from Trichoderma reesei.

The viscosities of the various cellulose derivatives and their hydrolyzates as described above were measured using a Haake-Rotovisco viscometer with sensor systems NV (Karlsruhe, Federal Republic of Germany) (Table 1). The viscosities were measured in water solutions at 25°C. Table 1 sets forth the concentrations (by weight) of a variety of solutions all having the same viscosity.

TABLE 1

Concentrations of cellulose derivatives and their respective hydrolyzates in solution all having a viscosity of 20 mPa.s (milli-Pascals-second) at 25°C.

Cellulose Derivative	Concentration (by weight)
Methylcellulose	2%
Methylcellulose hydrolyzate	5%
Hydroxypropylmethylcellulose	3%
Hydroxypropylmethylcellulose hydrolyzate	10%
Carboxymethylcellulose	2%
Carboxymethylcellulose hydrolyzate	20%

As the data in Table 1 indicate, the hydrolyzate of n cellulose derivative has a substantially lower viscosity than an equal amount by weight in aqueous solution of the cellulose derivative itself.

Example 4: Carboxymethylcellulose Chemical Hydrolysis

2 gms of carboxymethylcellulose (Blanose Cellulose Gum 7 LFD, Hercules Chemical Co., 92507, Rueil-Malmaison Cedar, France) was hydrolyzed for about one hour in 100 ml of 1M sulphuric acid solution at about 100°C. After hydrolysis the solution was cooled to about room temperature, neutralized to about pH 6 with 25 ml of 25% (w/w) of NaOH solution and freeze-dried. This hydrolysis treatment produced a mixture of polymers containing less than about 4% by weight of saccharides (cellobiose and glucose). The viscosity (and average DP) of this hydrolyzate is similar to the viscosities (and average DP) of the hydrolyzates produced by the enzymatic treatments described above utilizing enzymes derived from Trichoderma reesei.

Carboxymethyl cellulose (CMC) hydrolyzates can be prepared by enzymatic, chemical or physical methods as disclosed in U.S. Patent Applications Serial Nos. 07/309,387, 07/370,629 and 07/464,291. CMC hydrolyzates used in present invention have the average degree of polymerization in the range of 5 to 500, based on the viscosity average molecular weight. The viscosity average molecular weights of the CMC hydrolyzates were calculated using the Mark-Houwink equation:

$$[\eta] = KM_v^a$$

where $[\eta]$ is intrinsic viscosity, Mv is the viscosity average molecular weight of the polymer and K and a are hydrodynamic constants caracteristic of the particular polymer-solvent system. The values of K and a for CMC, which were used in this study, were K = 0.043 in 0.2 M NaCl and a = 0.76 in 0.2 M NaCl as described in Brown and Henley, Studies on Cellulose Derivatives Part IV. The Configuration of the Polyelectrolyte in Sodium Chloride Solutions, Macromol. Chem., Vol. 79, 68-88 (1964). It is noted that a variety of methods for determining average molecular weights exist, and therefore the values of average molecular weights determined, as well as the average DP values calculated from them, depend upon the experimental method and the basis for calculation. CMC hydrolysates described in this invention have an intrinsic viscosity of between 50 ml. per gram to 3ml. per gram, when determined in 0.2M sodium chloride. The CMC hydrolysates have the viscosity value in the range of from 5 to 100 mPa.s, when measured in 20% (by weight) solution at 25°C with shear rate $584 s^{-1}$ using a Haake Viscotester, VI 500 with sensor system NV (Karlsruhe, Federal Republic of Germany).

The Mark-Houwink exponent, a, is indicative of the conformation of the polymer chain in solution. The conformation of the polymer chain in solution may be classified as an 1) impermeable dense sphere, 2) random coil, e.g. semi-permeable or free draining, and 3) rodlet or rod-like. Mark-Houwink exponents of 0.002 to about

0.5 correspond to dense spheres, exponents of about 0.5 to about 0.8 correspond to semi-permeable random coils, exponents of 0.8 to about 1.2 correspond to free draining random coils and exponents of about 1.2 to about 2 correspond to rodlets or rod-like oligomers or polymers.

In an embodiment of this invention, the degradation product of the polysaccharide derivative comprises a mixture of oligomers of the polysaccharide having a Mark-Houwink exponent of at least 1.5 at an NaCl concentration of about 0.005N to about 0.5N. This NaCL concentration range is typically used when measuring Mark-Houwink exponents. The salt content of foodstuffs may also typically fall into this range.

CMC raw material (Mw>15,000 Daltons) has Mark-Houwink exponents of 0.83-0.97, indicating a free draining random coil conformation. In the random coil conformation, polymer coils are confined by the intra-chain interactions; therefore less change is seen in the Mark-Houwink exponent within the same range of ionic strength. However, when the weight average molecular weight is less than 15,000 Daltons, the CMC chain is not sufficiently long to form a winding coil, the polymer chain is no longer subjected to the constraint of intra-chain interactions, and a chain of free strip or rod-like configuration may form. When the ionic strength is low, the electrostatic repulsion force becomes dominant due to the negative charge of the carboxymethyl groups, and the polymer assumes its most stiff rod-like conformation with the highest value of the Mark-Houwink exponents. When the ionic strength increases, the negative charge of carboxymethyl groups is shielded, the repulsion forces between the neighbouring groups are reduced, and the polymer chains relax, yielding a lower Mark-Houwink exponent.

The experimentally determined data show that the molecular weight and chain conformational characteristics of the most preferred cellulose derivative oligomeric mixtures used in the invention, i.e. mixtures comprising a significant or substantial portion of oligomers of rod-like conformation, are distinctly different from those of undegraded cellulose derivatives. As shown by the experimentally determined Mark-Houwink a values listed in Table 2 below for weight average molecular weights, M_W, of CMC at less than about 15,000 daltons (a=1.58 to 2.07), the literature value of a=0.74 for CMC is erroneous with respect to CMC having a M_W of less than about 15,000 daltons. These experimentally determined data quantitatively indicate that relatively short chain CMC assumes a rod-like configuration as opposed to a free draining random coil conformation of the undegraded polymer.

TABLE 2

Mark-Houwink Equations for CMC (25°C)

NaCl Concentration (N)	Weight Average Molecular Weight >15,000	Weight Average Molecular Weight <15,000
0.005	$[\eta]=0.0069M_w^{0.97}$	$[\eta]=0.02\times10^{-5}M_w^{2.07}$
0.010	$[\eta]=0.0084M_w^{0.94}$	$[\eta]=0.17\times10^{-5}M_w^{1.82}$
0.050	$[\eta]=0.0090M_w^{0.91}$	$[\eta]=0.83\times10^{-5}M_w^{1.63}$
0.100	$[\eta]=0.0116M_w^{0.88}$	$[\eta]=1.18\times10^{-5}M_w^{1.59}$
0.200	$[\eta]=0.0182M_w^{0.83}$	$[\eta]=2.00\times10^{-5}M_w^{1.55}$
0.500	$[\eta]=0.0179M_w^{0.83}$	$[\eta]=1.21\times10^{-5}M_w^{1.58}$

Furthermore, the most preferred oligomeric mixtures according to the invention have a relatively narrow range of molecular weights, i.e. relatively monodispersed, having a polydispersity index (M_W/M_n, weight average molecular weight divided by number average molecular weight) of less than about 2.0 and typically less than about 1.8. The weight average molecular weights and number average molecular weights of a variety of CMC hydrolysate samples of different degree of hydrolysis were measured and the polydispersity index of all

such hydrolysates was calculated as ranging between about 1.1 and about 1.9. Therefore, the oligomers in a most preferred mixture of oligomers extend over a relatively narrow range of M_W and, even as to mixtures having an average molecular weight at or near the upper limit of M_W where the oligomers may begin to assume a random coil configuration, are comprised of a significant portion, preferably a majority, of oligomers having a rod-like configuration.

In the experimental determination of M_W values, CMC solutions were prepared in 0.2N NaCl solution at pH of 7. The solutions were passed through an HPLC column, and the light intensity was detected by multiangle laser light scattering using a Wyatt Technology, multiangle laser light scattering instrument, model DAWN-F. The flow rate was 0.2 ml/min. The concentrations of the solutions were detected by refractometer, and the sensitivity of the refractometer was 64. The weight average molecular weights, M_W, were determined using appropriate computer software.

Example 5: <u>Treatment of Paper with Polymers derived from Carboxymethyl cellulose (CMC)</u>

Ten percent of carboxylic cellulose hydrolyzate (intrinsic viscosity = 31.4 ml per gram) dispersion was prepared with deionized water by stirring overnight. The process was carried out by dipping Whatman No. 1 filter paper in the hydrolyzate dispersion in water for 5 minutes. After dipping, the papers were dried in an oven overnight. Three paper samples (hydrolyzate treated, water treated, and untreated papers) were tested for tensile strength, strain limit, modulus, and water and oil spreading. For the tensile test, paper was cut to 50 x 2 mm and loaded in the grip of an Instron Universal Testing Machine (Model 1122, Canton MA 02021).

<u>Results</u>

After dipping into hydrolyzate solution, the treated paper was dried and tested. (Table 3).

Table 3. The Change in Properties* of Paper Treated with Carboxymethyl Cellulose Hydrolyzate (CMC)

Sample Paper	Maximum Tensile Strength (atm)	Tangential Modulus (atm/%)	Strain Limit (%)
CMC Hydrolyzate #1	286	168	3.6
CMC Hydrolyzate #2	385	184	4.2
CMC Hydrolyzate #3	297	211	3.0
Water	120	73	3.9
Untreated	160	90	2.7

* Values are the average of 10 tests for each sample.

Force-elongation tests were performed with a cross-head speed of 5 mm min^{-1}, a chart speed of 500 mm min^{-1}, and a maximum load of 2000g_f. FIGS. 1, 2, 3 for hydrolyzate-treated water-treated, and untreated papers, respectively. The resultant values of the maximum tensile strength before rupturing of treated paper showed a 2 to 3 fold increase over untreated or water treated papers when the paper was treated with the hydrolyzate. Also, the strain limit and modulus increased by dipping paper in hydrolyzate (Table 3). Dipping paper in water alone decreased the mechanical strength and increased the strain limit (Table 3).

Water and oil spreading on the papers were also tested (Table 4). Paper dipped in the water did not show any difference in water spreading compared to untreated paper. However, it showed more spreading of oil compared to untreated paper. Hydrolyzate-dipped paper showed much less water spreading than untreated paper.

Table 4. Water and oil spreading* on treated and untreated papers

Sample	Water spreading[1] (diameter, mm)	Oil spreading[2] (diameter, mm)
Carboxymethyl cellulose hydrolyzate-treated	13	26
Water-treated	21	25
Untreated	20	23

* Average of Triplicate (± s.e.)

1 Measured diameter 5 minutes after spotting 20μl of water.

2 Measured diameter 30 minutes after spotting 20μl of oil.

Example 6: Treatment of Paper with Polymers derived from Carboxymethyl Starch (CMS)

Five percent carboxymethyl starch (CMS) and carboxymethyl starch hydrolyzate (CMSH) dispersions were prepared with deionized water. Two sets of dispersions were made; one was mixed (10 minutes) at room temperature and the other at 90°C (to achieve gelatinization). The coating process was carried out by dipping Whatman No. 1 filter paper in each polymer dispersion for 5 minutes. After dipping, the papers were dried in an oven overnight. The paper samples were tested for tensile strength, strain limit and modulus. For the tensile test, paper was cut to 50 x 2 mm and loaded in the grip of an Instron Universal Testing Machine (Model 1122, Canton, MA 02021).

In both sets of samples prepared at room temperature and at 90°C, the paper treated with carboxymethyl starch hydrolyzate had higher tensile strength and strain limit than the paper treated with carboxymethyl starch of higher molecular weight. (Table 5). This shows, that the mechanical properties of the paper can be improved more using carboxymethyl starch or lower molecular weight. Also the modulus was higher when the paper was treated with carboxymethyl starch hydrolyzates suggesting an increase in the stiffness of the paper (Table 5).

Table 5. The Change in Properties* of Paper Treated with Carboxymethyl Cellulose Hydrolyzate (CMC)

Sample Paper	Maximum Tensile Strength (atm)	Strain Limit (%)	Tangential Modulus (atm/%)
CM Starch (room temp.)	79	3.2	48
CM Starch (90°C)	80	4.9	43
CM Starch Hydrolyzate (CMSH) (room temp.)	209	5.2	130
CM Starch Hydrolyzate CMSH (90°C)	234	6.9	117

Example 7: Hydrolyzed Polysaccharide Derivatives as Dewatering Aids

Polysaccharide derivatives or their hydrolyzates were prepared and dissolved in water. After stirring for 10 minutes, the solution was added to furnish. The final mixture contained furnish (0.106% w/v solid) and 0.0053% (w/v) polysaccharide derivatives or their hydrolyzates. The mixture was mixed for 10 minutes and poured on basement paper which serves as a screen. The amount of water drained was recorded for the determination of dewatering rate and final water content was measured. The furnish was dried in the oven and used in the tensile strength test.

Drainage tests for furnish treated with charged polysaccharides and with their hydrolyzates showed initial drainage rates higher than that of furnish alone. (FIG. 4).

The amount of drained water (i.e. an index of dewatering) and the water content of the furnish (i.e. an index of draining) treated with charged polysaccharide derivatives and their hydrolyzates are shown in Table 6.

Table 6

Furnish Treatment	Amount of Water Drained (ml)	Weight of Retained Water (g) (Final Water Content)
CMC Hydrolyzate	95	5.3
CMC	92	4.5
CM Starch Hydrolyzate	94	6.2
CM Starch	94	5.4
Control (Furnish)	93	5.0

Tensile strength tests showed that the furnish treated with charged polysaccharide hydrolyzates gave higher tensile strength and tangential modulus than those tested with high molecular weight charged polysaccharides (Table 7).

Table 7

Sample Furnish Treatment	Maximum Tensile Strength (atm)	Strain Limit (%)	Modulus (atm %)
CMC Hydrolyzate	114.0	4.7	60
CMC	75.8	5.5	33
CM Starch Hydrolyzate	100.0	4.7	58
CM Starch	85.7	4.3	46
Control (Furnish)	88.4	4.7	51

Therefore, this experiment shows that polysaccharide derivatives and their hydrolyzate increase the rate of dewatering in the early stage of drainage. Particularly, the polysaccharide derivative hydrolyzates of the invention significantly improve the mechanical properties of the pulp product.

Example 8:

Polysaccharides or their hydrolyzates were prepared and dissolved in a warm water (80°C, CM starch and its hydrolyzate) or room temperature water (CMC and its hydrolyzate). After stirring for 10 minutes, the solution was mixed with $Ca(CO_3)_2$ solution. After stirring for 10 minutes, the mixture was added to furnish. The mixture

contained furnish with 0.106% (w/v) solid, 0.106% (w/v) $Ca(CO_3)_2$, and 0.00575% (w/v) polysaccharides or their hydrolyzates. The test for dewatering was repeated. The draining rates were faster in those mixtures containing hydrolyzate than those of high molecular weight polysaccharides (Figure 5).

The amount of drained water, and the final water content of the samples treated with charged polysaccharides and their hydrolyzates are shown in Table 8. Furnish and $Ca(CO_3)_2$ treated with hydrolyzates showed a higher dewatering rate, retaining less water than furnish and $Ca(CO_3)_2$ treated with higher molecular weight polysaccharide derivatives.

Table 8

Furnish Mixture Treatment	Amount of Water Drained (ml)	Weight of Retained Water (g) (Final Water Content)
CMC Hydrolyzate	98	4.3
CMC	90	5.5
CM Starch Hydrolyzate	94	6.4
CM Starch	89	7.4

The furnish mixture thus produced were dried in an oven and the tensile strength was tested. The test results showed that the samples treated with charged polysaccharide hydrolyzates had a higher tensile strength and tangential modulus than those treated with high molecular weight charged polysaccharide for both CMC and CM starch (Table 9).

Table 9

Sample Paper	Maximum Tensile Strength (atm)	Strain Limit (%)	Tangential Modulus (atm/%)
CMC Hydrolyzate	81.2	4.5	43
CMC	61.4	4.4	35
CM Starch Hydrolyzate	101.7	5.0	61
CMS	85.7	5.6	49
Control (Furnish)	88.4	4.7	51

Claims

1. A paper product treated with a mixture of oligomers derived by degradation of a polysaccharide derivative, a majority of said oligomers having a degree of polymerization and molecular weight such that the oligomer conforms to a rod-like configuration.

2. A paper product comprising cellulose fibres, or synthetic or mineral fibres or a mixture thereof, the said fibres being treated with a mixture of oligomers derived by degradation of a polysaccharide derivative, the mixture of oligomers having an average degree of polymerization in the range of between about 3 and 500.

3. A paper product according to claim 1 or 2 wherein the paper product is coated with the mixture of oligomers or has the mixture of oligomers incorporated therein.

4. A paper product according to claim 1, 2 or 3 wherein the polysaccharide derivative is a cellulose derivative of a starch derivative, carragenan, pullulan, pustulan, alginate, laminarin, guar gum, gum arabic, inulin, pectin, whelan, rhamsan, gellan, xanthan, scleroglucan, zooglan, methylan, chitin, cyclodextrin or chitosan.

5. A paper product according to claim 1, 2 or 3, wherein the polysaccharide derivative is substituted by carboxymethyl, methyl, hydroxypropyl, methylethyl, hydroxyethyl, hydroxymethylethyl, hydroxypropylmethyl, sulfate, carboxylic acid, carboxylic acid ester, or pyruvate.

6. A paper product according to claim 5, wherein the mixture of oligomers has an average degree of polymerization in the range of about 5 to about 100.

7. A paper product according to claim 5 wherein the mixture of oligomers has an average degree of polymerization in the range of about 5 to 50 and a rod-like configuration.

8. A paper product according to any one of claims 1 to 7 wherein the mixture of oligomers has an average molecular weight of less than about 15000 daltons.

9. A paper product according to any one of claims 1 to 8 wherein the mixture of oligomers has a molecular weight distribution such that its polydispersity index is less than 2 and the mixture contains less than 25% by weight of mono- and di-saccharides.

10. A paper product according to any of claims 1 to 9 having a tangential modulus of about 43 atm/percent to about 211 atm/percent, preferably 117 atm/percent to 211 atm/percent.

11. A paper product according to any of claims 1 to 10, having a tensile strength of about 81.2 atm to about 385 atm, preferably 209 to 385 atm.

12. A paper product according to any of claims 1 to 11, having a strain limit of about 3.0 percent to about 6.9 percent, preferably 3.0 to 5.0 percent.

13. A method of making paper of increased tear strength which comprises incorporating into said paper during or after its manufacture a mixture of oligomers derived by degradation of a polysaccharide derivative, said mixture having an average degree of polymerization in the range of between about 4 and about 500.

14. A method of making paper of increased tear strength which comprises incorporating into said paper during or after its manufacture a mixture of oligomers derived by degradation of a polysaccharide derivative, a majority of said oligomers having a degree of polymerization and molecular weight such that the oligomer conforms to a rod-like configuration.

15. A method according to claim 13 or 14, wherein the mixture of oligomers has an average degree of polymerization in the range of about 5 to about 100.

16. A method according to claim 13 or 14, wherein the mixture of oligomers has an average degree of polymerization in the range of about 5 to 50 and a rod-like configuration.

17. A method according to any one of claims 13 to 16, wherein the polysaccharide derivative is a cellulose derivative of a starch derivative, carragenan, pullulan, pustulan, alginate, laminarin, guar gum, gum arabic, scleroglucan, inulin, pectin, whelan, rhamsan, gellan, xanthan, zooglan, methlan, chitin, cyclodextrin or chitosan.

18. A method according to any one of claims 13 to 17 wherein the polysaccharide derivative is substituted by carboxyethyl, methyl, hydroxypropyl, methylethyl, hydroxyethyl, hydroxymethylethyl, hydroxypropylmethyl, sulfate, carboxylic acid, carboxylic acid ester, or pyruvate.

19. A method according to any one of claims 13 to 18 wherein the mixture of oligomers has an average molecular weight of less than about 15000 daltons.

20. A method according to any one of claims 13 to 19 wherein the mixture of oligomers has a molecular weight distribution such that its polydispersity index is less than 2 and the mixture contains less than 25% by weight of mono- and di-saccharides.

21. A method according to any one of claims 13 to 20, wherein one or more dyes, colorants, wet-strength agents and defoamers are also incorporated into the paper.

22. A method according to any one of claims 13 to 21, wherein the mixture of oligomers is incorporated by coating the paper by dipping, spraying or rolling, or by including the mixture in the furnish.

Fig. 1

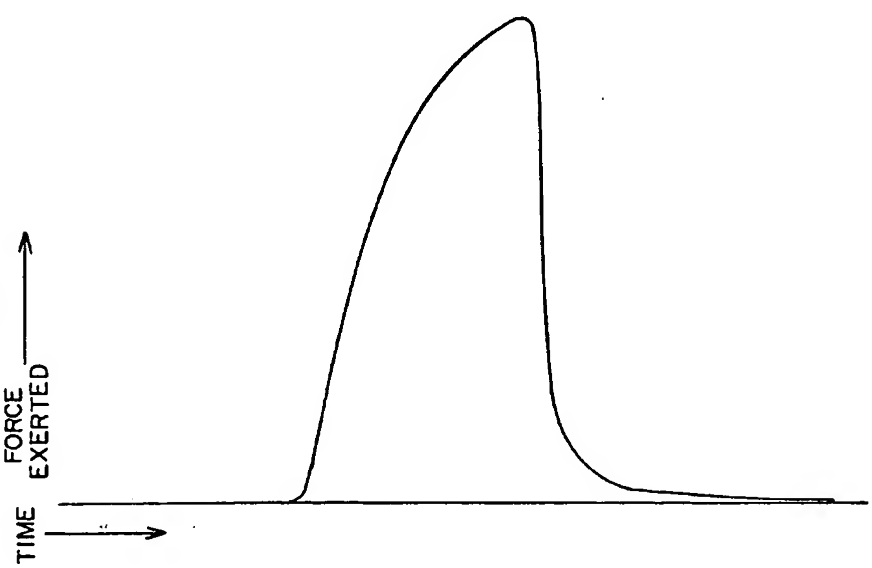


Fig. 2

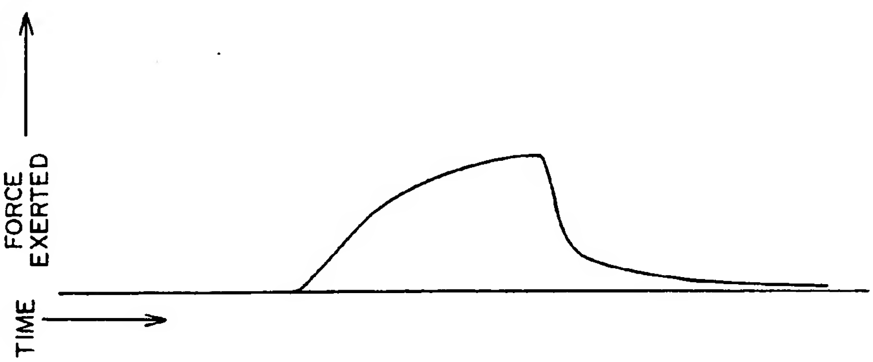
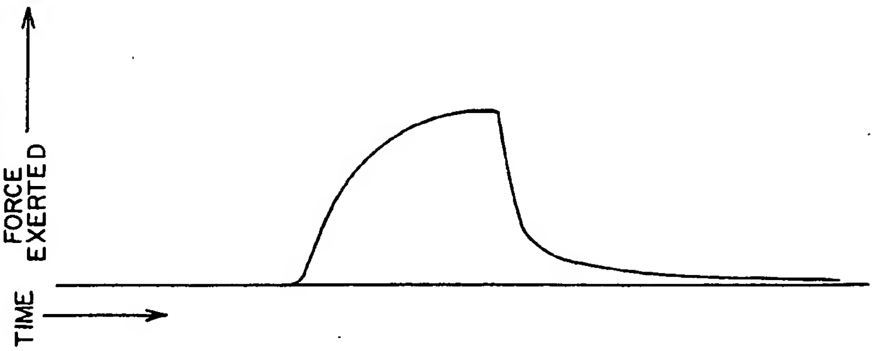
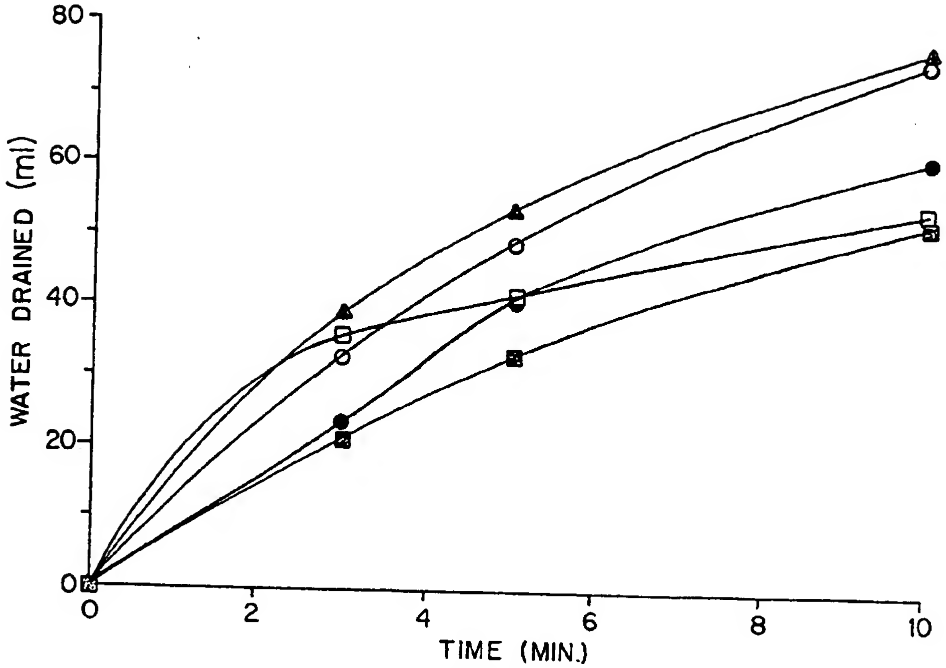


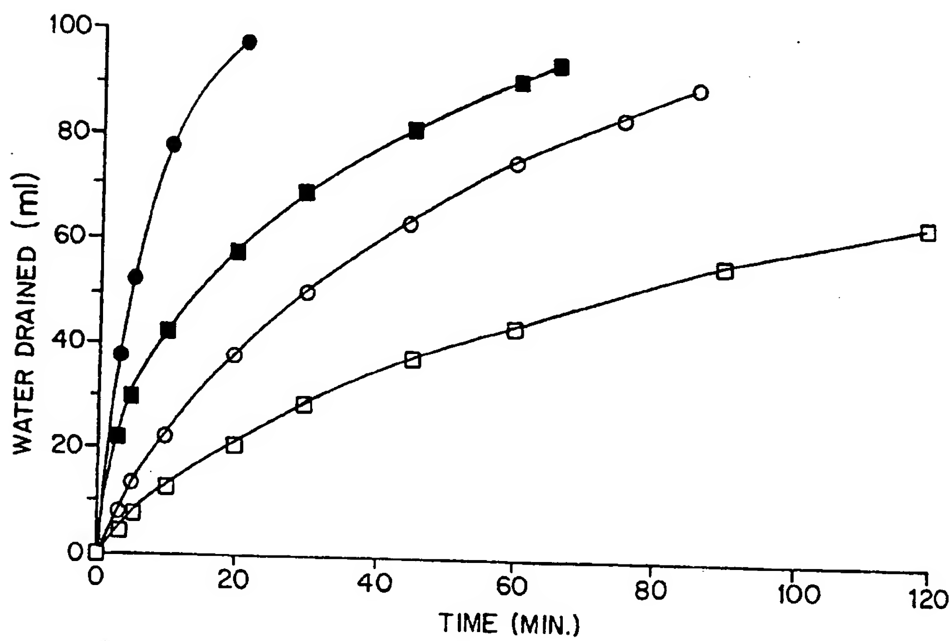
Fig. 3





80
60
40
20
0
WATER DRAINED (ml)
0
2
4
6
8
10
TIME (MIN.)

Fig. 4



100
80
60
40
20
0
WATER DRAINED (ml)
0
20
40
60
80
100
120
TIME (MIN.)

Fig. 5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 7417

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 382 576 (ALKO LTD) * Page 2, line 1 - page 8, line 31; page 5, lines 34-42 * & CA-A-2 009 675 (10-08-1990) (Cat. X)	1-8,13-19	D 21 H 17/24 D 21 H 17/00 D 21 H 21/18
A	EP-A-0 301 372 (BASF AG) * The whole document *	1-22	
A	EP-A-0 147 380 (MONSANTO CO.) * The whole document *		
A	DE-A-2 636 951 (GÜNTHER WAGNER PELIKAN-WERKE GmbH) * The whole document *		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 21 H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-11-1991	SONGY O.M-L.A.

CATEGORY OF CITED DOCUMENTS

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